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Theoretical study on the outer- and inner-valence ionization spectra of H_2O, H_2S and H_2Se using the SAC-CI general-*R* method

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The outer- and inner-valence ionization spectra of the Group VI hydrides H_2O, H_2S and H_2Se below the double-ionization threshold were studied by the SAC-CI (symmetry-adapted-cluster configuration-interaction) general-*R* method. The SAC-CI method quite accurately reproduced the experimental spectra of these hydrides and gave detailed characterizations of the shake-up states. Several unknown satellite peaks were predicted. The shake-up state which includes excitations to the Rydberg orbitals was found to be very important for describing the satellite peaks of these hydrides. A detailed inner-valence satellite spectrum of H_2Se is theoretically proposed prior to any experimental observation. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1367372]

I. INTRODUCTION

Many satellite peaks are found in the inner-valence region of ionization spectra. These peaks are of considerable interest since they reflect electron correlations in molecules. The recent development of high-resolution x-ray photoelectron spectroscopy (XPS), synchrotron radiation photoelectron spectroscopy (SRPES) and electron momentum spectroscopy (EMS) has enabled detailed and intensive experimental studies of these peaks.

The inner-valence region of the Group VI hydrides H_2O, H_2S and H_2Se is an interesting target for these spectroscopies, and many satellite peaks have been observed. Potts and Prince[1] reported He II PES of the outer-valence spectra of Group VI hydrides. For H_2O and H_2S, careful and detailed experimental studies on the satellite peaks have been performed by SRPES,[2,3] XPS[4,5] and EMS.[6–10] There is little experimental information available on the inner-valence ionization spectrum of H_2Se, and only the EMS spectrum[11] up to 23 eV has been reported.

Theoretically, the outer- and inner-valence satellite peaks of these hydrides have been investigated in some detail by the symmetry-adapted-cluster configuration-interaction (SAC-CI) method,[12,13] by the Green's function method[14,15] and by the multi-reference single and double CI (MR-SDCI) method.[8,10] A systematic study on the satellite spectra of these hydrides using the extended $3h$-$2v$-$1p$ or $4h$-$3v$ CI method has also been reported.[16] However, since these shake-up peaks are both numerous and complicated, their assignments in the inner-valence region are still difficult. It is important to perform reliable calculations with extended basis sets including sufficient electron correlations, especially for the assignment of high-lying shake-up states.

In the present study, we examined the ionization spectra in the outer- and inner-valence region of the Group VI hydrides H_2O, H_2S and H_2Se using the SAC-CI method. The SAC-CI method[17–19] has been successfully applied to several molecular spectroscopic problems including ionization spectroscopy.[20–24] There are two standards in the SAC-CI method with respect to the choice of the linked operators, *R*. In the SAC-CI SD (single double)-*R* method, single and double excitation operators are adopted for *R* operators, while the SAC-CI general-*R* method[25,26] also involves triple and higher excitation operators. The latter method is designed to describe multiple-electron processes with high accuracy, and has been shown to be useful for studying large numbers of states in the ionization spectrum.[27–30] Details of the general-*R* method can be found in Ref. 25.

Computational details are given in Sec. II. In Sec. III we give results and a discussion, and in Sec. IV we give concluding remarks.

II. COMPUTATIONAL DETAILS

We used experimental geometries[31] for H_2O, H_2S and H_2Se, and studied vertical ionization. For H_2O, the O–H bond length R(O–H) is 0.956 Å and the HOH angle ∠HOH is 105.2°. For H_2S, R(S–H) is 1.328 Å and ∠HSH is 92.2°. For H_2Se, R(Se–H) is 1.460 Å and ∠HSeH is 91°. Basis sets were derived from the correlation-consistent polarized valence triple-zeta (cc-pVTZ),[32] augmented with three *s*-, *p*- and *d*-type Rydberg functions for O, S and Se atoms [α_s(O)=0.059; 0.017; 0.0066, α_p(O)=0.059; 0.015; 0.0054, α_d(O)=0.059; 0.016; 0.0032, α_s(S)=0.041; 0.027; 0.0173, α_p(S)=0.041; 0.025; 0.0015, α_d(S)=0.088; 0.029; 0.0011, α_s(Se)=0.033; 0.013; 0.0055, α_p(Se)=0.039; 0.016, 0.0065, α_d(Se)=0.096; 0.040; 0.016]. The Rydberg functions for O and S atoms were taken from Ref. 33. The exponentials of the Rydberg functions for the Se atom were determined by extrapolation of those of the cc-pVTZ. The *f*-type functions for O, S and Se atoms and the *d*-type function for a H atom of cc-pVTZ were not included in our calculations because they did not significantly contribute to describing the ionized states of these hydrides. The resulting basis sets are $(13s8p5d/5s2p)/[7s6p5d/3s2p]$,

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TABLE I. The SAC-CI general-*R* dimensions[a] for the ionized states of H_2O, H_2S and H_2Se.

State	Singles	Doubles	Triples	Quadruples	Total
H_2O					
$^2A_1$	2/2	292/292	17 199/22 042	55 553/88 7654	73 046/909 990
$^2A_2$	0/0	209/212	13 217/21 554	33 653/88 8334	47 079/910 100
$^2B_1$	1/1	238/242	13 266/21 698	31 391/88 8644	44 896/910 585
$^2B_2$	1/1	262/262	15 275/21 898	42 043/88 7224	57 581/909 385
H_2S					
$^2A_1$	2/2	292/292	15 668/22 042	114 305/887 654	130 267/909 990
$^2A_2$	0/0	209/212	12 778/21 554	76 409/888 334	89 396/910 100
$^2B_1$	1/1	242/242	12 213/21 698	72 062/888 644	84 518/910 585
$^2B_2$	1/1	262/262	13 551/21 898	78 995/887 224	92 809/909 385
H_2Se					
$^2A_1$	4/4	1210/1367	31 738/28 0148	64 798/31 877 014	97 750/32 158 533
$^2A_2$	1/1	789/1187	20 742/27 8196	42 860/31 881 094	64 392/31 903 024
$^2B_1$	2/2	956/1252	23 922/27 8734	40 240/31 882 844	65 120/32 162 832
$^2B_2$	2/2	1050/1297	24 996/27 9534	41 931/31 874 324	67 979/32 155 157

[a]Dimension after perturbation selection/before perturbation selection.

$(18s12p5d/5s2p)/[8s7p5d/3s2p]$ and $(23s16p12d/5s2p)/[9s8p6d/3s2p]$ for H_2O, H_2S and H_2Se, respectively.

The main peaks were calculated by the SAC-CI general-*R* and SD-*R* methods. To describe the shake-up peaks, it is important to include higher-than-double excitation operators in the linked operators. This was confirmed by a series of recent applications.[27–30] Therefore, we applied the SAC-CI general-*R* calculation for the outer- and inner-valence shake-up states. Since most of the shake-up states of these hydrides are described by two-electron processes, higher excitation operators were limited up to quadruple. The active space consists of 4 occupied MOs and 63 unoccupied MOs for H_2O and H_2S, and 9 occupied and 63 unoccupied MOs for H_2Se, where the $1s$ orbital of O, $1s$, $2s$ and $2p$ orbitals of S, and $1s$, $2s$, $3s$, $2p$ and $3p$ orbitals of Se were frozen as cores. To reduce the computational effort, perturbation selection is carried out for linked operators higher-than-double excitations.[21] For the ground state, the threshold for the linked doubles is $\lambda_g = 1\times10^{-7}$ a.u. and the unlinked terms are written as the products of the important linked terms whose SDCI coefficients are larger than 0.005. For the ionized states, the threshold for the linked single and double excitation operators is $\lambda_e = 1\times10^{-7}$ a.u., and that for the linked triple and quadruple operators is $\lambda_e = 1\times10^{-6}$ a.u. for H_2O, and $\lambda_e = 5\times10^{-6}$ a.u. for H_2S and H_2Se. In the perturbation selection, a state-selection scheme is used. The thresholds of the CI coefficients for calculating the unlinked operators in the SAC-CI method are 0.005 and 1×10^{-8} for the *R* and *S* operators, respectively.

Ionization cross-sections were calculated using the monopole approximation[34,35] to estimate the relative intensities of the peaks. Both initial- and final-state correlation effects are included. In particular, the intensity of the $^2A_2$ state arises only from the initial-state correlation effect.

HF SCF calculations were performed using GAUSSIAN 98[36] and SAC/SAC-CI calculations were performed using the SAC-CI96 program system.[37]

III. RESULTS AND DISCUSSION

A. H_2O

The outer- and inner-valence ionization spectra of H_2O up to the double-ionization threshold (about 42 eV) were studied by the SAC-CI general-*R* method. The outer-valence main peaks were also calculated by the SAC-CI SD-*R* method. Forty ionized states were calculated for A_1 symmetry and 20 states were calculated for other symmetries, since most of the shake-up states with considerable intensity are associated with A_1 symmetry. The SAC-CI general-*R* dimensions are summarized in Table I, together with those before the perturbation selection. Since most of the shake-up states under consideration are described predominantly by two-electron processes, the SD-CI solutions are used for the reference state in the perturbation selection. The resultant dimensions are 73046, 47079, 44896 and 57581 for the $^2A_1$, $^2A_2$, $^2B_1$ and $^2B_2$ states, respectively.

The Hartree–Fock (HF) electronic configuration of H_2O is written as

$$(\text{core})^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2.$$

The ionization spectrum of H_2O in both the outer- and inner-valence regions by the SAC-CI general-*R* method is presented in Fig. 1, in comparison with the dipole $(e,2e)$ spectrum.[6] In the theoretical spectrum, the calculated pole strengths are shown by solid vertical lines and are convoluted using a Gaussian with a fwhm of 2.0 eV estimated by averaging fwhms of three main peaks of the dipole $(e,2e)$ spectrum. The theoretical spectrum reproduces the main peaks and the satellites quite accurately. First, we discuss three main peaks: $(1b_1^{-1})$, $(3a_1^{-1})$ and $(1b_2^{-1})$ states. Table II shows the ionization potentials (IPs) and monopole intensities of these peaks by the SAC-CI method with the experimental IPs by He II PES[1] and EMS.[7] The SAC-CI SD-*R* results, 12.33, 14.56 and 18.90 eV, compare well with the experimental values of 12.62, 14.74 and 18.51 eV for $(1b_1^{-1})$, $(3a_1^{-1})$ and $(1b_2^{-1})$, respectively. The inclusion of

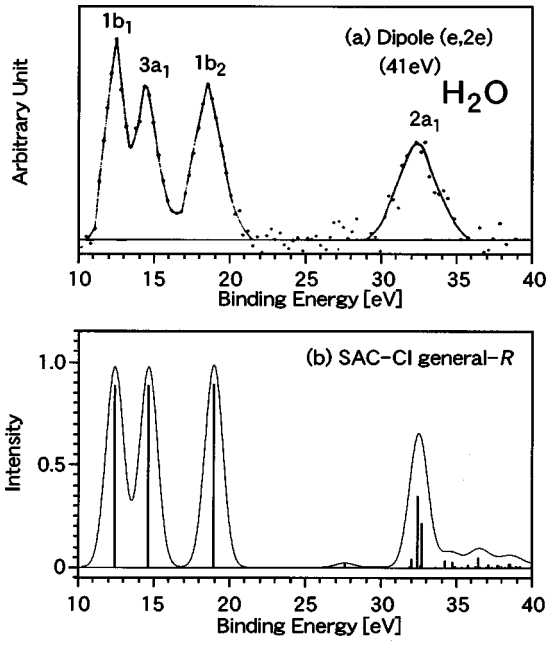

FIG. 1. The valence ionization spectra of H_2O by (a) the dipole $(e,2e)$ spectrum (Ref. 6), and (b) the SAC-CI general-R method. In the theoretical spectrum, the calculated pole strength of each peak is shown as a solid vertical line and is convoluted with a fwhm of 2.0 eV.

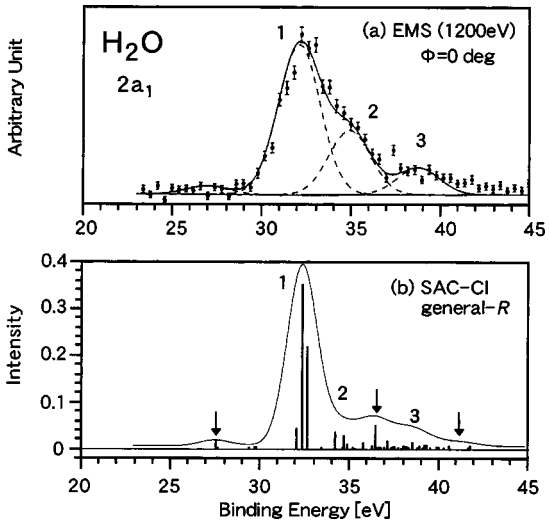

FIG. 2. The inner-valence spectra of H_2O in 25–43 eV region by (a) EMS (Ref. 7) and (b) the SAC-Cl general-R method. In the theoretical spectrum, the calculated pole strength of each peak is shown as a solid vertical line and is convoluted with an experimental width of 2.77 eV fwhm estimated from EMS (Ref. 7). Arrows show the predicted bands by the SAC-CI general-R method.

higher excitation operators R does not greatly affect the main-peak positions or their intensities, which is consistent with other examples.[27–30]

Next, the satellite peaks in the inner-valence region are discussed. In Fig. 2, the innervalence satellite spectrum by the SAC-CI general-R method is compared with EMS.[7] The theoretical spectrum is convoluted with an experimental width of 2.77 eV fwhm estimated from the EMS spectrum.[7] Note that this convolution includes the Frank–Condon width and energy resolution of the spectrometer. Table III shows the IPs, monopole intensities and main configurations of the inner-valence satellite peaks, whose IPs are up to 42 eV with intensities greater than 0.005. The outer-valence satellite lines accompanied by $(1b_2^{-1})$, $(3a_1^{-1})$ and $(1b_1^{-1})$ are also shown in Table III, though most of them are calculated to have very low intensities. The IPs and intensities observed by EMS are also presented in Table III.

Three satellite bands numbered 1–3 were observed by EMS, and they are shown by Gaussian deconvolution with a dashed line. Three $^2A_1$ states calculated at 32.05, 32.37 and 32.66 are assigned to the strong band 1 centered at 32.2 eV. The total pole strength of these states is calculated to be 0.612, which is in good agreement with the experimental intensity of 0.580. These three states are mainly described by a linear combination of $(2a_1^{-1})$ and two electron process, such as $(1b_1^{-2}na_1)$ and $(3a_1^{-2}na_1)$, whose strong interaction causes the split peaks. In a previous SAC-CI SD-R study,[12] only one $^2A_1$ state was calculated at 32.39 eV, and was mainly described as $(2a_1^{-1})$, which did not interact with the shake-up configurations. The MR-SDCI calculation[8] gave two states to band 1 at 33.1 and 33.6 eV. In the energy region around band 1, the $(1b_1^{-1})$ outer-valence satellite peak was also calculated at 32.64 eV with a low intensity of 0.005. However, this state does not directly contribute to the observable pole strength in EMS measured at azimuthal angle $\phi=0$. Bowagan *et al.*[7] suggested that the EMS spectrum at $\phi=0$ probed very low momentum components, which tended to emphasize the ionization from ''*s*-type'' orbitals, and did not sufficiently ascertain the outer-valence satellite peak with a ''*p*-type'' character.

Three $^2A_1$ states calculated at 34.23, 34.74 and 34.89 eV are attributed to band 2 of medium pole strength at 35.0 eV. Considerable mixing of the shake-up states including excitations to Rydberg orbitals is found for these states. A previous SAC-CI study also gave the shake-up state at 34.89 eV to this band, and the MR-SDCI calculation placed this at 34.2 eV.

We also found the medium band at around 37 eV. Five shake-up states were calculated at 35.80, 36.27, 36.44, 37.12 and 37.74 eV with a total pole strength of 0.094: these shake-up states are mainly characterized as $(3a_1^{-1}nb_21b_2^{-1})$, $(1b_2^{-1}nb_21b_1^{-1})$ and $(1b_1^{-2}na_1)$. This medium band is also assigned to band 2 at 35.0 eV. The total pole strength of eight shake-up states at 34–38 eV is 0.168, which agrees well with the experimental value of 0.180. We consider that band 2 actually consists of two peaks, and this splitting is caused by the strong interaction between the

TABLE II. Ionization potential (IP) (in eV) and monopole intensity for the main peaks of H_2O calculated by the SAC-CI SD-R and general-R methods.

	Exptl.		SAC-CI SD-R		SAC-CI general-R	
State	He II PES[a]	EMS[b]	IP	Int.	IP	Int.
$(1b_1)^{-1}$	12.62	12.20	12.33	0.870	12.38	0.884
$(3a_1)^{-1}$	14.74	15.00	14.56	0.871	14.61	0.884
$(1b_2)^{-1}$	18.51	18.60	18.90	0.882	18.92	0.893

[a]Reference 1.
[b]Reference 7.

TABLE III. Ionization potential (IP) (in eV), monopole intensity and main configurations of the outer- and inner-valence satellite peaks of H_2O calculated by the SAC-CI general-*R* method.

Exptl.[a]			SAC-CI general-*R*			
No.	IP	Int.	IP	Int.	State	Main configurations ($C>0.3$)
	⋯	⋯	27.56	0.018	$^2A_1$	$0.54(1b_1^{-2}12a_1)-0.45(1b_1^{-2}16a_1)+0.38(1b_1^{-2}8a_1)$
1	32.20	0.580	32.05	0.045	$^2A_1$	$0.38(1b_1^{-2}12a_1)-0.34(1b_1^{-2}16a_1)-0.33(1b_1^{-2}6a_1)$
			32.37	0.350	$^2A_1$	$0.59(2a_1^{-1})-0.31(3a_1^{-2}12a_1)$
			32.64	0.005	$^1B_1$	$0.41(1b_1^{-2}6b_1)+0.31(1b_1^{-1}8b_2 1b_2^{-1})$
			32.66	0.217	$^2A_1$	$0.46(2a_1^{-1})$
2	35.00	0.180	34.23	0.034	$^2A_1$	$0.45(1b_1^{-2}13a_1)$
			34.74	0.029	$^2A_1$	$0.63(1b_1^{-1}6b_1 3a_1^{-1})+0.45(3a_1^{-1}6b_1 1b_1^{-1})$ $+0.43(1b_1^{-1}4b_1 3a_1^{-1})+0.39(3a_1^{-1}7b_1 1b_1^{-1})$
			34.89	0.011	$^2A_1$	$0.42(1b_1^{-1}7b_1 3a_1^{-1})+0.40(3a_1^{-1}6b_1 1b_1^{-1})$ $+0.32(1b_1^{-1}5b_1 3a_1^{-1})$
	⋯	⋯	35.80	0.013	$^1B_1$	$0.49(1b_2^{-1}6b_2 1b_1^{-1})+0.45(1b_2^{-1}8b_2 1b_1^{-1})$
			36.27	0.007	$^2A_1$	$0.30(1b_1^{-1}4b_1 3a_1^{-1})$
			36.44	0.053	$^2A_1$	$0.45(3a_1^{-1}8b_2 1b_2^{-1})+0.42(3a_1^{-1}6b_2 1b_2^{-1})$
			37.12	0.017	$^2A_1$	$0.41(1b_2^{-1}8b_2 3a_1^{-1})-0.38(3a_1^{-2}13a_1)$ $+0.37(1b_2^{-1}6b_2 3a_1^{-1})+0.31(3a_1^{-1}8b_2 1b_2^{-1})$
			37.74	0.004	$^2A_1$	$0.52(1b_1^{-2}10a_1)-0.39(1b_1^{-2}9a_1)+0.33(1b_1^{-2}4a_1)$
3	38.90	0.095	38.00	0.007	$^2A_1$	$0.30(1b_1^{-1}3b_1 3a_1^{-1})$
			38.51	0.014	$^2A_1$	$0.34(1b_1^{-2}10a_1)-0.31(1b_1^{-2}4a_1)$
			38.52	0.014	$^2A_1$	$0.37(1b_1^{-2}4a_1)-0.35(1b_1^{-2}8a_1)$
			38.96	0.005	$^2A_1$	$0.37(1b_1^{-2}13a_1)$
			39.26	0.007	$^2A_1$	$0.37(1b_2^{-2}12a_1)-0.33(1b_2^{-2}16a_1)$
	⋯	⋯	40.57	0.007	$^2A_1$	$0.79(1b_1^{-1}3a_2 1b_2^{-1})+0.76(1b_2^{-1}3a_2 1b_1^{-1})$ $+0.42(1b_1^{-1}2a_2 1b_2^{-1}+0.41(1b_2^{-1}2a_2 1b_1^{-1})$
			41.78	0.006	$^2A_1$	$0.54(3a_1^{-1}7b_2 1b_2^{-1})+0.51(1b_2^{-1}7b_2 3a_1^{-1})$

[a]EMS (Ref. 7): the corresponding spectrum is shown in Fig. 2(a).

shake-up configurations including the excitations to Rydberg orbitals. A more detailed experimental study is necessary in this energy region. One of these satellites, the $(1b_1^{-1})$ outer-valence satellite, was calculated at 35.80 eV with an intensity of 0.013.

The weak broad band 3 at 38.90 eV is assigned to five shake-up states calculated at 38.00, 38.51, 38.52, 38.96 and 39.26 eV. These states are mainly described as $(1b_1^{-2}na_1)$ including excitations to valence orbitals na_1. In a previous SAC-CI study, a shake-up state at 40.70 eV was assigned to band 3. MR-SDCI also calculated this band to be at 39.5 eV.

We found two peaks in the inner-valence region which were not reported in the EMS study. In the lower-energy region below the strong band 1, we calculated a weak peak at 27.56 eV. The EMS spectrum also has a weak peak at around 27.0 eV. MR-SDCI gave a weak peak at 29.0 eV, while this state was not obtained in the previous SAC-CI calculation. This state is mainly characterized by simultaneous ionization-excitation $(1b_1^{-2}na_1)$, and the inclusion of higher excitations in the *R* operators is necessary to describe this state. Furthermore, the experimental spectrum also seems to have a very weak peak at around 41 eV. Two shake-up states with a low intensity calculated at 40.57 and 41.78 eV are assigned to this peak. The total pole strength of these states is 0.013. For these two shake-up states, considerable mixing of the excitations to Rydberg orbitals with a_2 and b_2 symmetries is found.

B. H_2S

The outer- and inner-valence ionization spectra of H_2S up to about 33 eV were studied by the SAC-CI general-*R* method, since some double-ionization thresholds lie in the energy range of 31.7–37.8 eV.[38] To examine the spectrum in this energy region, 40 $^2A_1$ ionized states were calculated, and 20 states were calculated for other symmetries. The calculational dimensions are 130267, 89396, 84518 and 92809 for the $^2A_1$, $^2A_2$, $^2B_1$ and $^2B_2$ states, respectively, as shown in Table I.

The HF electronic configuration of H_2S is calculated as

$$(\text{core})^{10}(4a_1)^2(2b_2)^2(5a_1)^2(2b_1)^2.$$

In Fig. 3, the valence ionization spectrum of H_2S by the SAC-CI general-*R* method is compared with the results by SRPES.[3] Though the cross-section of the peaks in the SRPES depends on the character of the states, our method reproduces the spectrum very accurately. Table IV shows the IPs and intensities of the three main peaks by the SAC-CI method. The experimental IPs by He II PES,[1] EMS[10] and XPS[4,5] are also given. Though there are some discrepancies in the experimental IPs, both the SAC-CI SD-*R* and general-*R* methods adequately reproduce the experimental values: the calculated values of 10.19, 13.26 and 15.62 eV by the former method are comparable to the He II PES values of 10.47, 13.33 and 15.47 eV, respectively.

Next, the theoretical inner-valence satellite spectrum of H_2S is compared with those of SRPES,[2] XPS[5] and EMS.[10] Relative cross-sections are reported in the XPS study and the normalized intensities are given for comparison. Table V shows the calculated IPs, monopole intensities and main configurations of the inner- and outer-valence satellite peaks of H_2S together with the IPs by three experiments. They are shown for states up to about 33 eV with calculated intensities

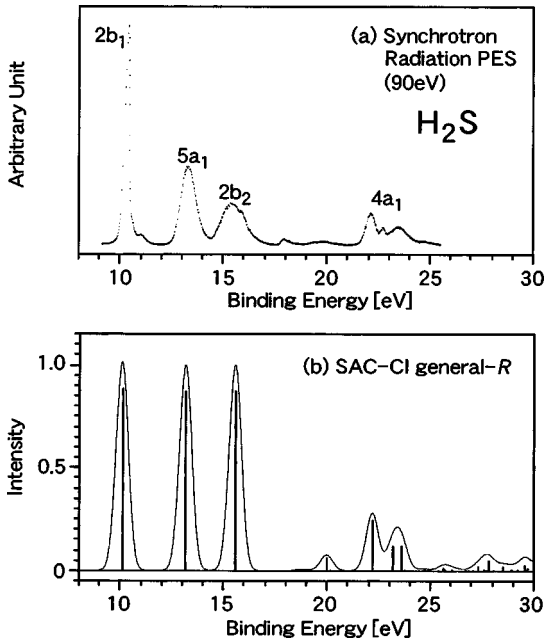

FIG. 3. The valence ionization spectra of H_2S by (a) synchrotron radiation PES. (Ref. 3) and (b) the SAC-CI general-*R* method. In the theoretical spectrum, the calculated pole strength of each peak is shown as a solid vertical line and is convoluted with a fwhm of 1.2 eV.

greater than 0.005. Some outer-valence satellite states are also given, even though they have small intensities, especially within 22–25 eV. Note that there are still several outer- and inner- valence satellites that are not given in Table V.

The inner-valence SRPES[2] is presented in Fig. 4. Since the resolution and deconvolution of the spectrum is more detailed in SRPES and XPS than in EMS, we first compare the results by SRPES and XPS: the two experiments gave similar results. In SRPES, 11 satellite bands were observed in the inner-valence region as shown in Table V, where band 7 was proposed to be comprised of three peaks. Consequently, 13 bands were confirmed and their IPs were determined by Gaussian deconvolution of the composite band.

A weak peak (band 1) was observed at 19.60 eV (SRPES) and 19.90 eV (XPS) below the strong peak, and was attributed to the ''shake-down'' peak.[2,39] The SAC-CI general-*R* method gave a state at 20.00 eV. This state is characterized as $(2b_1^{-2}na_1)$, which is consistent with the analysis given in Ref. 5. This state borrows intensity from the $(4a_1^{-1})$ state, and the calculated intensity of 0.059 is comparable to the XPS value of 0.065. The simplified ADC(4) calculation[15] also gave a weak peak at 19.22 eV.

In the energy region of 21–25 eV, intensive experimental studies were performed by SRPES and XPS. SRPES gave six bands numbered 2 to 7, as seen in Fig. 4(b). We assign the state calculated at 22.21 eV with a strong intensity (0.241) to band 2 at 22.0 eV, which is the strongest in the inner-valence region. XPS and EMS also gave strong bands at 22.08 and 22.37 eV, respectively, with an XPS intensity of 0.210. In the simplified ADC(4), this state was calculated at 21.51 eV. This state is described as a linear combination of $(4a_1^{-1})$ and $(2b_1^{-2}na_1)$, in which the two-electron process mainly accompanies the excitations to both valence and Rydberg orbitals.

The six bands observed from 22.5 to 24 eV were very close and their assignments are still not definitive. Bands 3 and 4 are narrow. Neither EMS nor $(e,2e)$[9] has shown band 3. The three experimental findings[2,5,40] (width, β parameter and the branching ratio as a function of photon energy) suggested that bands 2, 5 and 6 [Fig. 4(b)] corresponded to $(4a_1^{-1})$ inner-valence satellite states, while bands 3 and 4 arose
from states of a different character and were assigned to be the outer-valence satellites. Accordingly, we obtained the $(2b_2^{-1})$ outer-valence satellite state at 22.24 eV for band 3, although its intensity was quite low. On the contrary, the $(4a_1^{-1})$ inner-valence satellite calculated at 22.47 eV was assigned to band 3 by the simplified ADC(4) method. In the present result, the $^2A_1$ state calculated at 23.20 eV may also be a candidate for band 3 on the basis of the intensity.

For the medium peaks around 23 eV, the SRPES study gave three bands 4–6 at 23.05, 23.31 and 23.57 eV evaluated by deconvolution [Fig. 4(b)]. The $^2A_1$ state calculated at 23.20 eV with an intensity of 0.117 is attributed to band 4 at 23.05 eV, and the two outer-valence satellites of $(2b_1^{-1})$ at 23.21 and 23.47 eV with low intensities are attributed to band 5 at 23.31 eV and the $^2A_1$ state at 23.62 eV with an intensity of 0.118 is attributed to band 6 at 23.57 eV. These twinning peaks with the medium pole strength correspond to the $(4a_1^{-1})$ inner-valence satellites. From the β spectrum, the existence of the $(4a_1^{-1})$ inner-valence satellite has been confirmed in the energy region around 23.5 eV. Both of these twinning states are described by a linear combination of $(4a_1^{-1})$ and $(2b_1^{-2}na_1)$, and we found considerable mixing of the two-electron process including excitations to the Ry-

TABLE IV. Ionization potential (IP) (in eV) and monopole intensity for the main peaks of H_2S calculated by the SAC-CI SD-*R* and general-*R* methods.

	Exptl.				SAC-CI SD-*R*		SAC-CI general-*R*	
State	He II PES[a]	EMS[b]	XPS[c]	XPS[d]	IP	Int.	IP	Int.
$(2b_1)^{-1}$	10.47	10.50	10.46	10.30	10.19	0.861	10.11	0.884
$(5a_1)^{-1}$	13.33	13.10	13.43	13.20	13.26	0.852	13.18	0.870
$(2b_2)^{-1}$	15.47	15.60	15.55	15.10	15.62	0.851	15.58	0.871

[a]Reference 1.
[b]Reference 10.
[c]Reference 5.
[d]Reference 4.

TABLE V. Ionization potential (IP) (in eV), monopole intensity and main configurations of the outer- and inner-valence satellite peaks of H_2S calculated by the SAC-CI general-*R* method.

	Exptl.				SAC-CI general-*R*			
No.[a]	IP[a]	IP[b]	IP[c]	Int.[c]	IP	Int.	State	Main configurations ($C>0.3$)
	⋯	⋯	∼18	0.018	18.86	0.005	$^2B_2$	$0.64(2b_1^{-2}8b_2)-0.52(2b_1^{-2}6b_2)$ $-0.32(2b_1^{-2}7b_2)$
1	19.60	19.63	19.90	0.059	20.00	0.065	$^2A_1$	$0.57(2b_1^{-2}15a_1)-0.43(2b_1^{-2}11a_1)$
2	22.00	22.37	22.08	0.210	22.21	0.241	$^2A_1$	$0.49(4a_1^{-1})-0.35(2b_1^{-2}16a_1)$ $+0.34(2b_1^{-2}11a_1)-0.33(2b_1^{-2}7a_1)$
3	22.54	⋯	22.68	0.060	22.24	0.0003	$^2B_1$	$0.50(5a_1^{-1}15a_1 2b_1^{-1})-0.42(5a_1^{-1}11a_1 2b_1^{-1})$
4	23.05	⋯	23.00	0.030	23.20	0.117	$^2A_1$	$0.36(4a_1^{-1})+0.44(2b_1^{-2}17a_1)$ $-0.42(2b_1^{-2}12a_1)+0.36(2b_1^{-2}16a_1)$
5	23.31[d]	⋯	⋯	⋯	23.21	0.0006	$^2B_1$	$0.47(2b_1^{-1}15a_1 5a_1^{-1})-0.42(2b_1^{-1}11a_1 5a_1^{-1})$ $+0.41(5a_1^{-1}15a_1 2b_1^{-1})-0.31(5a_1^{-1}15a_1 2b_1^{-1})$
					23.47	0.0003	$^2B_1$	$0.50(2b_1^{-2}8b_1)+0.41(2b_2^{-1}8b_2 2b_1^{-1})$ $+0.33(2b_1^{-2}6b_1)-0.33(2b_2^{-1}6b_2 2b_1^{-1})$ $+0.31(2b_1^{-1}8b_2 2b_2^{-1})$
6	23.57	24.07	23.43	0.190	23.62	0.118	$^2A_1$	$0.34(4a_1^{-1})-0.51(2b_1^{-2}17a_1)$ $-0.34(2b_1^{-2}13a_1)$
7	23.72	⋯	⋯	⋯	23.76	0.001	$^2A_2$	$0.63(2b_1^{-2}2a_2)+0.43(2b_1^{-2}3a_2)$
	23.98	⋯	⋯	⋯	23.95	0.002	$^2B_2$	$0.57(5a_1^{-2}8b_2)-0.44(5a_1^{-2}6b_2)$
	24.50	⋯	24.90	0.025	24.22	0.001	$^2B_1$	$0.44(2b_2^{-1}8b_2 2b_1^{-1})-0.38(2b_1^{-2}6b_1)$
					24.69	0.007	$^2B_1$	$0.57(2b_1^{-2}5b_1)+0.57(2b_1^{-2}7b_1)$
					24.70	0.001	$^2B_1$	$0.43(5a_1^{-1}16a_1 2b_1^{-1})+0.36(5a_1^{-1}7a_1 2b_1^{-1})$
					24.72	0.002	$^2A_1$	$0.58(2b_1^{-2}10a_1)-0.52(2b_1^{-2}14a_1)$
	⋯	⋯	⋯	⋯	25.65	0.014	$^2A_1$	$0.46(5a_1^{-2}15a_1)-0.35(5a_1^{-2}11a_1)$
					25.73	0.008	$^2A_1$	$0.47(2b_1^{-1}8b_1 5a_1^{-1})+0.35(2b_1^{-1}6b_1 5a_1^{-1})$ $+0.33(2b_2^{-1}8b_2 5a_1^{-1})$
					26.03	0.004	$^2B_1$	$0.42(2b_1^{-1}11a_1 5a_1^{-1})-0.30(2b_1^{-1}16a_1 5a_1^{-1})$
					26.34	0.003	$^2A_1$	$0.60(5a_1^{-1}8b_1 2b_1^{-1})+0.47(5a_1^{-1}6b_1 2b_1^{-1})$
8	26.70	26.89	27.20	0.123	27.33	0.020	$^2A_1$	$0.40(2b_1^{-2}13a_1)-0.36(5a_1^{-1}8b_2 2b_2^{-1})$ $-0.33(2b_1^{-1}3a_2 2b_2^{-1})$
					27.60	0.005	$^2A_1$	$0.56(2b_1^{-2}8a_1)+0.41(2b_1^{-2}12a_1)$ $+0.31(2b_1^{-1}5b_1 5a_1^{-1})$
	⋯	⋯	27.90	0.200	27.85	0.050	$^2A_1$	$0.37(2b_2^{-1}6b_2 5a_1^{-1})-0.35(2b_2^{-1}8b_2 5a_1^{-1})$ $+0.30(2b_1^{-1}6b_1 5a_1^{-1})$
9	28.40	28.83	28.65	0.138	28.54	0.019	$^2A_1$	$0.50(2b_2^{-1}3a_2 2b_1^{-1})+0.39(2b_2^{-1}2a_2 2b_1^{-1})$ $+0.33(5a_1^{-1}6b_1 2b_1^{-1})$
					28.93	0.006	$^2A_1$	$0.26(5a_1^{-2}16a_1)+0.25(2b_1^{-1}3a_2 2b_2^{-1})$
					29.23	0.009	$^2A_1$	$0.26(2b_1^{-1}4b_1 5a_1^{-1})+0.26(2b_1^{-2}12a_1)$ $+0.26(2b_1^{-2}8a_1)+0.26(2b_1^{-1}3a_2 2b_2^{-1})$
10	29.60	⋯	30.05	0.128	29.55	0.005	$^2A_1$	$-0.41(5a_1^{-1}5b_1 2b_1^{-1})+0.32(2b_1^{-1}7b_1 5a_1^{-1})$ $+0.31(5a_1^{-1}7b_1 2b_1^{-1})$
					29.60	0.027	$^2A_1$	$0.37(5a_1^{-2}16a_1)-0.31(2b_1^{-1}2a_2 2b_2^{-1})$
					29.68	0.005	$^2B_2$	$0.61(2b_1^{-1}5b_1 2b_2^{-1})+0.50(2b_1^{-1}7b_1 2b_2^{-1})$ $+0.37(2b_1^{-2}3b_2)+0.33(2b_2^{-1}7b_1 2b_1^{-1})$
					29.72	0.011	$^2A_1$	$0.38(2b_1^{-2}13a_1)+0.35(2b_1^{-2}11a_1)$ $+0.33(2b_1^{-2}16a_1)$
11	31.00	30.51	⋯	⋯	30.06	0.006	$^2A_1$	$0.49(5a_1^{-1}4b_1 2b_1^{-1})+0.35(2b_1^{-1}6b_1 5a_1^{-1})$ $-0.34(5a_1^{-2}16a_1)$
					30.19	0.006	$^2A_1$	$0.48(2b_1^{-2}18a_1)-0.37(2b_1^{-1}4b_1 5a_1^{-1})$ $+0.31(5a_1^{-1}4b_1 2b_1^{-1})$
					30.65	0.041	$^2A_1$	$0.62(2b_1^{-1}4b_1 5a_1^{-1})-0.36(5a_1^{-1}8b_1 2b_1^{-1})$ $+0.35(5a_1^{-1}4b_1 2b_1^{-1})$
					30.92	0.023	$^2A_1$	$0.43(2b_2^{-2}15a_1)-0.37(2b_2^{-2}11a_1)$
					31.19	0.016	$^2A_1$	$0.29(5a_1^{-1}4b_1 2b_1^{-1})+0.28(2b_1^{-1}7b_1 5a_1^{-1})$ $-0.28(2b_1^{-1}6b_1 5a_1^{-1})-0.27(2b_1^{-1}8b_1 5a_1^{-1})$
	⋯	32.72	⋯	⋯	32.13	0.010	$^2A_1$	$0.61(2b_1^{-1}6b_1 5a_1^{-1})+0.56(5a_1^{-1}6b_1 2b_1^{-1})$ $-0.51(2b_1^{-1}4b_1 5a_1^{-1})-0.49(5a_1^{-1}4b_1 2b_1^{-1})$
					32.24	0.005	$^2A_1$	$0.51(2b_1^{-1}1a_2 2b_2^{-1})+0.48(2b_2^{-1}1a_2 2b_1^{-1})$ $+0.46(2b_2^{-1}5b_2 5a_1^{-1})+0.39(2b_2^{-1}7b_2 5a_1^{-1})$
					32.44	0.009	$^2A_1$	$0.49(2b_1^{-1}1a_2 2b_2^{-1})-0.47(2b_2^{-1}5b_2 5a_1^{-1})$ $+0.41(2b_2^{-1}1a_2 2b_1^{-1})-0.40(2b_2^{-1}7b_2 5a_1^{-1})$

[a]SRPES (Ref. 2): the corresponding spectrum is shown in Fig. 4. Six bands observed from 22.5 to 24 eV were obtained by fitting a broad band with Gaussians (Ref. 2); see Fig. 4(b).
[b]EMS (Ref. 10): the corresponding spectrum is shown in Fig. 5(a).
[c]XPS (Ref. 5).

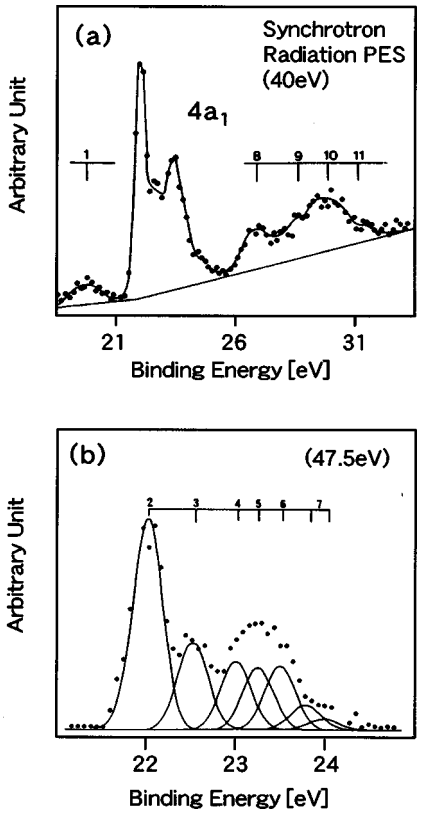

FIG. 4. The satellite spectra of H_2S by the synchrotron radiation PES cited from Ref. 2, (a) in the whole inner-valence region up to double ionization threshold, and (b) in the energy region of 21–25 eV.

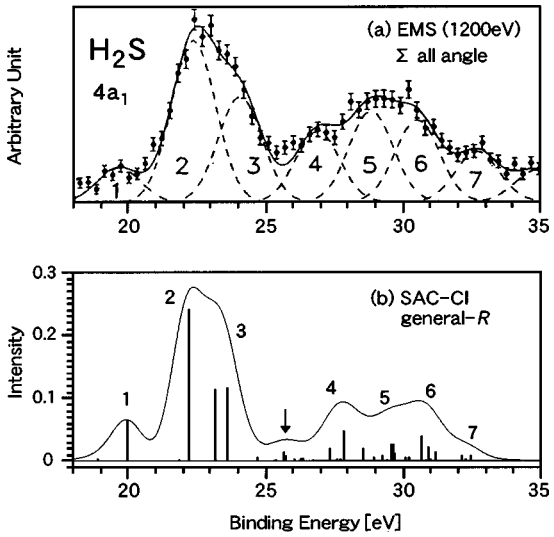

FIG. 5. The inner-valence spectra of H_2S in the 18–33 eV region by (a) EMS (Ref. 10) and (b) the SAC-CI general-*R* method. In the theoretical spectrum, the calculated pole strength of each peak is shown as a solid vertical line and is convoluted with an experimental width of 1.9 eV fwhm estimated from EMS (Ref. 10). Arrows show the predicted bands by the SAC-CI general-*R* method.

dberg orbitals. The *d*-type Rydberg basis sets are very important for describing these peaks. XPS also gave three peaks in the 22.5–24 eV energy region: the normalized intensities were evaluated to be 0.060, 0.030 and 0.190 for the peaks at 22.68, 23.00 and 23.43 eV, respectively. The total pole strength of 0.280 was consistent with those of the $^2A_1$ twinning states calculated as 0.235. An experimental analysis predicted that the valence state $(5a_1^{-2}na_1)$ should have appeared at about 25 eV for band 6. Accordingly, this state was calculated at 25.65 eV, however, it had a low intensity and thus should be attributed to the new band discussed below.

Three peaks at 23.72, 23.98 and 24.50 eV were attributed in SRPES to the two small bands (band 7) around 24 eV in Fig. 4(b). The SAC-CI general-*R* method gave the assignment for each peak. To the peak at 23.72 eV, we assign a $^2A_2$ state calculated at 23.76 eV, where its intensity is purely due to the initial-state correlation. The $(2b_2^{-1})$ outer-valence satellite at 23.95 eV was assigned to the state at 23.98 eV. For the peak at 24.50 eV, we assign four shake-up states with low intensities at 24.22, 24.69, 24.70 and 24.72 eV. The $^2A_1$ state at 24.72 eV with a low intensity of 0.002 is characterized as $(1b_1^{-2}na_1)$, which includes valence-excitation. Three other states at 24.22, 24.69 and 24.70 correspond to the $(2b_1^{-1})$ outer-valence satellites. The total pole strength is calculated as 0.014, which is comparable to the XPS value of 0.025.

In this energy region of 21–25 eV, the MR-SDCI and simplified ADC(4) methods gave only three or four states and did not completely explain bands 2–7. This is the first study to propose theoretical assignments for the eight peaks observed in this region.

To each weak band 8–11 observed at 26.7, 28.4, 29.6 and 31.0 eV, we assign several shake-up states in good agreement with the experimental results. In the SAC-CI general-*R* method, three states calculated at 27.33, 27.60 and 27.85 eV are attributed to band 8 at 26.7 eV, three states at 28.54, 28.93 and 29.23 eV are attributed to band 9 at 28.4 eV, four states at 29.55, 29.60, 29.68 and 29.72 eV are attributed to band 10 at 29.6 eV and five states at 30.06, 30.19, 30.65, 30.92 and 31.19 eV are attributed to band 11 at 31.00 eV, respectively. These shake-up states are mainly due to the shake-up process which includes excitations to the Rydberg orbitals. The calculated intensities for these peaks are low compared with the results by XPS, which is consistent with the results of other theoretical works.[15,16]

In Fig. 5, the inner-valence satellite spectrum calculated by the SAC-CI general-*R* method is shown along with the EMS spectrum for a detailed comparison. The theoretical spectrum is convoluted with an experimental width of 1.9 eV fwhm which was reported to give a good fit to the experimental spectrum. The SAC-CI general-*R* method quite accurately reproduced the shape of the EMS spectrum. EMS did not completely confirm the 11 bands observed by SRPES, and especially the outer-valence satellites in the energy region of 21–25 eV. In this energy region, only two bands were observed at 22.37 and 24.07 eV. EMS suggested that these states have a dominant *s*-type character, and from this analysis, it appears that the band at 22.37 eV (mark 2) in EMS corresponds to band 2 at 22.00 eV in SRPES, while the band at 24.07 eV (mark 3) in EMS corresponds to bands 4 and 6 in SRPES. The ionization characters of these states by the SAC-CI general-*R* method are consistent with those by these two experimental methods.

In EMS, a weak band (mark 7) was observed at 32.72

eV, though this band lay above the double-ionized state of $(2b_1^{-2})$ at 31.7 eV. We tentatively assign the three states calculated at 32.13, 32.24 and 32.44 eV to this band. The main configurations of these states are described by $(2b_1^{-1}nb_15a_1^{-1})$, $(5a_1^{-1}nb_12b_1^{-1})$, $(2b_2^{-1}nb_25a_1^{-1})$, $(2b_1^{-1}na_22b_2^{-1})$, and $(2b_2^{-1}na_22b_1^{-1})$, which mainly include excitations to the Rydberg orbitals. Although a few bands were observed at higher binding energies in EMS, the calculation in this energy region is inadequate because of the double-ionization threshold and the limited number of Rydberg orbitals included. Neither ADC(4) nor MR-SDCI extended into this energy region.

Finally, we found a new satellite band in the energy region at around 26 eV which has not yet been reported in an experimental study. This band consists of four shake-up states calculated at 25.65, 25.73, 26.03 and 26.34 eV, where the shake-up state at 25.65 eV corresponds to the valence state $(5a_1^{-1}na_1)$, and the state at 26.03 eV arises from the outer-valence satellites for $(2b_1^{-1})$. EMS also seems to give a shoulder below the peak (mark 4) at 26.89 eV, as seen in Fig. 5(a). Furthermore, in the lower-energy region below the first band at around 20 eV, an outer-valence satellite of $(2b_2^{-1})$ was calculated at 18.86 eV with a low intensity of 0.005. This peak is assigned to the very small band near 18 eV in SRPES as seen in Fig. 3(a) and in XPS.

C. H_2Se

The outer- and inner-valence ionization spectra of H_2Se up to the double-ionization threshold of about 30 eV, were studied by the SAC-CI general-*R* method. Forty ionized states were examined for A_1 symmetry, and 20 states were examined for other symmetries. Table I summarizes the SAC-CI general-*R* dimensions.

The HF configuration of H_2Se is given by

$$(\text{core})^{28}(8a_1)^2(4b_2)^2(9a_1)^2(4b_1)^2.$$

Figure 6 shows the ionization spectrum of H_2Se by the SAC-CI general-*R* method, in comparison with the $(e,2e)$ spectrum.[11] An experimental linewidth of 1.4 eV fwhm, which was used for the deconvolution of the $(e,2e)$ spectrum, is adopted for the theoretical spectrum. In Table VI, the IPs and monopole intensities of the outer-valence main peaks of H_2Se are summarized for the SAC-CI method, and compared with the experimental IPs by He II PES[1] and $(e,2e)$ spectroscopy. The calculated IPs of 9.56, 12.72 and 14.65 eV by the SAC-CI SD-*R* method agree well with the experimental values.

To our knowledge, the detailed experimental spectrum in the inner-valence region of H_2Se has not yet been reported. Two bands at 21.0 and 21.5 eV were observed by the $(e,2e)$ spectroscopy[11] and one band was seen at 21 eV by He II PES.[1] The relative intensities were not determined in these experiments. A theoretical spectrum was calculated using the $3h$-$2v$-$1p$ CI method.[16]

The H_2Se satellite spectrum in the $(8a_1^{-1})$ inner-valence region by the SAC-CI general-*R* method is presented in Fig. 7. Table VII shows the calculated IPs, monopole intensities and main configurations of the inner-valence satellite peaks of H_2Se. They are shown for states up to about 30 eV with calculated intensities greater than 0.005. In the SAC-CI general-*R* method, eight satellite bands were proposed by

TABLE VI. Ionization potential (IP) (in eV) and monopole intensity for the main peaks of H_2Se calculated by the SAC-CI SD-*R* and general-*R* methods.

	Exptl.		SAC-CI SD-*R*		SAC-CI general-*R*	
State	$(e,2e)$[a]	He II PES[b]	IP	Int.	IP	Int.
$(4b_1)^{-1}$	10.20	9.88	9.56	0.865	9.57	0.895
$(9a_1)^{-1}$	13.00	12.93	12.72	0.860	12.73	0.880
$(4b_2)^{-1}$	14.70	14.62	14.65	0.850	14.70	0.867

[a]Reference 11.
[b]Reference 1.

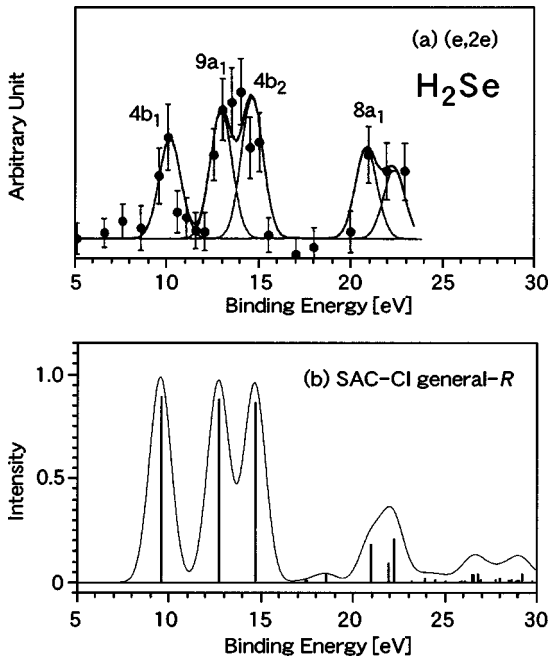

FIG. 6. The valence ionization spectra of H_2Se by (a) the $(e,2e)$ spectrum (Ref. 11) and (b) the SAC-CI general-*R* method. In the theoretical spectrum, the calculated pole strength of each peak is shown as a solid vertical line and is convoluted with an experimental width of 1.4 eV fwhm estimated from the $(e,2e)$ spectrum (Ref. 11).

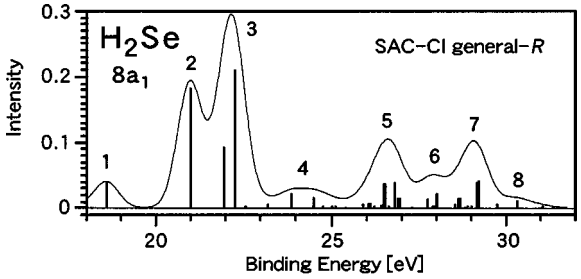

FIG. 7. The inner-valence spectra of H_2Se in the 18–32 eV region calculated by the SAC-CI general-*R* method. The calculated pole strength of each peak is shown as a solid vertical line and is convoluted with a fwhm of 1.4 eV. The eight bands numbered 1 to 8 are evaluated by the convolution of the peaks.

TABLE VII. Ionization potential (IP) (in eV), monopole intensity and main configurations of the outer- and inner-valence satellite peaks of H_2Se calculated by the SAC-CI general-*R* method.

Exptl.[a] IP	Exptl.[b] IP	SAC-CI general-*R* No.	IP	Int.	State	Main configurations ($C>0.3$)
⋯	⋯		17.46	0.009	$^2B_2$	$0.74(4b_1^{-2}8b_2)-0.49(4b_1^{-2}10b_2)$
⋯	⋯	1	18.57	0.039	$^2A_1$	$0.59(4b_1^{-2}16a_1)-0.49(4b_1^{-2}20a_1)+0.37(4b_1^{-2}12a_1)$
21.00	21.00	2	20.99	0.184	$^2A_1$	$0.42(8a_1^{-1})+0.43(4b_1^{-2}18a_1)$ $+0.36(4b_1^{-2}12a_1)-0.31(4b_1^{-2}22a_1)$
⋯	21.50	3	21.95	0.093	$^2A_1$	$0.30(8a_1^{-1})-0.59(4b_1^{-2}17a_1)-0.48(4b_1^{-2}21a_1)$
			22.25	0.210	$^2A_1$	$0.45(8a_1^{-1})-0.43(4b_1^{-2}18a_1)$
⋯	⋯	4	23.18	0.008	$^2B_1$	$0.56(4b_1^{-2}9b_1)+0.53(4b_1^{-2}7b_1)$
			23.89	0.022	$^2A_1$	$0.48(9a_1^{-2}16a_1)-0.39(9a_1^{-2}20a_1)$
			24.50	0.017	$^2A_1$	$0.41(4b_1^{-1}8b_19a_1^{-1})+0.33(4b_1^{-1}10b_19a_1^{-1})$
⋯	⋯	5	25.92	0.005	$^2B_2$	$0.50(4b_2^{-1}8b_14b_1^{-1})+0.46(4b_2^{-1}10b_14b_1^{-1})$
			26.10	0.006	$^2A_1$	$0.39(9a_1^{-1}8b_24b_2^{-1})-0.32(4b_1^{-1}4a_24b_2^{-1})$ $+0.32(4b_1^{-1}3a_24b_2^{-1})$
			26.47	0.005	$^2A_1$	$0.56(4b_1^{-1}7b_19a_1^{-1})+0.45(4b_1^{-1}9b_19a_1^{-1})$ $+0.38(9a_1^{-1}9b_14b_1^{-1})+0.34(9a_1^{-1}7b_14b_1^{-1})$
			26.52	0.036	$^2A_1$	$0.44(4b_2^{-1}8b_29a_1^{-1})-0.37(4b_2^{-1}3a_24b_1^{-1})$ $+0.34(4b_1^{-1}8b_19a_1^{-1})-0.31(4b_2^{-1}4a_24b_1^{-1})$
			26.79	0.039	$^2A_1$	$0.45(4b_2^{-1}3a_24b_1^{-1})-0.34(4b_1^{-2}10a_1)$ $+0.32(4b_2^{-1}4a_24b_1^{-1})$
			26.94	0.016	$^2A_1$	$0.38(4b_1^{-2}14a_1)-0.38(4b_1^{-2}10a_1)$ $-0.31(4b_2^{-1}3a_24b_1^{-1})$
⋯	⋯	6	27.75	0.014	$^2A_1$	$0.32(4b_1^{-1}6b_19a_1^{-1})-0.31(9a_1^{-1}6b_14b_1^{-1})$
			28.01	0.022	$^2A_1$	$0.38(9a_1^{-2}17a_1)$
			28.52	0.007	$^2A_1$	$0.39(9a_1^{-1}6b_14b_1^{-1})-0.36(9a_1^{-2}18a_1)$ $+0.36(4b_1^{-2}22a_1)$
			28.67	0.016	$^2A_1$	$0.48(4b_1^{-1}6b_19a_1^{-1})+0.46(9a_1^{-1}6b_14b_1^{-1})$ $-0.44(4b_1^{-2}22a_1)-0.34(4b_1^{-2}18a_1)$
⋯	⋯	7	29.00	0.005	$^2A_1$	$0.38(4b_2^{-2}16a_1)+0.32(4b_1^{-1}6b_19a_1^{-1})$ $-0.31(4b_2^{-2}20a_1)$
			29.17	0.040	$^2A_1$	$0.46(4b_1^{-1}5b_19a_1^{-1})-0.39(9a_1^{-1}6b_14b_1^{-1})$ $-0.37(4b_1^{-1}6b_19a_1^{-1})-0.34(9a_1^{-1}9b_14b_1^{-1})$
			29.23	0.041	$^2A_1$	$0.46(4b_1^{-1}6b_19a_1^{-1})+0.33(9a_1^{-1}7b_14b_1^{-1})$ $+0.31(4b_1^{-1}5b_19a_1^{-1})$
			29.74	0.006	$^2A_1$	$0.43(4b_2^{-1}2a_24b_1^{-1})$
⋯	⋯	8	30.34	0.011	$^2A_1$	$0.79(4b_1^{-1}2a_24b_2^{-1})+0.53(4b_2^{-1}2a_24b_1^{-1})$ $-0.39(4b_1^{-1}4a_24b_2^{-1})$

[a]He II PES (Ref. 1).
[b]$(e,2e)$ (Ref. 11): the corresponding spectrum is shown in Fig. 6(a).

Gaussian convolution of the peaks, which are numbered 1 to 8. The shape of the H_2Se spectrum appears to be very similar to that of H_2S.

The shake-up state at 18.57 eV below the strong peak was calculated as in the case of H_2O and H_2S. This band is mainly characterized as a two-electron process, $(4b_1^{-2}na_1)$. This band is denoted as band 1 and has not yet been observed experimentally.

The SAC-CI method calculated twinning bands with strong intensities at around 22 eV, which constitute bands 2 and 3. Band 2 calculated at 20.99 eV is assigned to the satellite peak at 21 eV observed by both $(e,2e)$ and He II PES. Band 3 consists of two shake-up states calculated at 21.95 and 22.25 eV with strong intensities of 0.093 and 0.210. We assign band 3 to the second peak 21.5 eV in the $(e,2e)$ spectrum. These twinning bands were mainly characterized as $(8a_1^{-1})$ and $(4b_1^{-2}na_1)$, in which considerable mixing of the shake-up configurations including excitations to the Rydberg orbitals is found. The Rydberg basis sets are important for describing these strong twinning bands, as in the case of H_2S.

For the higher energy region, no experimental spectra have been observed. Theoretical satellite bands 4 to 8 are proposed prior to any experiment. Many shake-up states were found in the energy region of 23–30 eV, as in the case of H_2O and H_2S.

Band 4 is composed of three shake-up states calculated at 23.18, 23.89 and 24.50 eV. Two $^2A_1$ states at 23.89 and 24.50 eV are described as $(9a_1^{-2}na_1)$ and $(4b_1^{-1}nb_19a_1^{-1})$, where $(9a_1^{-2}na_1)$ includes the excitations to the valence orbitals. Another state at 23.18 eV corresponds to the $(4b_1^{-1})$ outer-valence satellite peak. Band 5 consists of six shake-up states, which were calculated at 25.92, 26.10, 26.47, 26.52, 26.79 and 26.94 eV. The state at 25.92 eV corresponds to the $(4b_2^{-1})$ outer-valence satellite state. The others are $^2A_1$ states, which are characterized as a two-electron process including excitations to the Rydberg orbitals. Four shake-up

states calculated at 27.75, 28.01, 28.52 and 28.67 eV were assigned as band 6, four states at 29.00, 29.17, 29.23 and 29.74 eV were assigned as band 7, and a state at 30.34 eV was assigned as band 8. These shake-up states are also due to the shake-up process including excitations to the Rydberg orbitals.

Finally, the outer-valence satellite of $(4b_2^{-1})$ was also calculated at 17.46 eV with a low intensity of 0.009, as in the case of H_2S. No weak satellite peak in this region has been reported for the H_2Se ionization spectrum, experimentally or theoretically.

IV. CONCLUSION

The ionization spectra of the Group VI hydrides, H_2O, H_2S and H_2Se, were studied by the SAC-CI method in both the outer- and inner-valence regions. The SAC-CI method quite accurately reproduced the experimental spectra of these molecules wherever available.

In the outer-valence region, three main peaks of these hydrides were calculated and the experimental IPs were well reproduced by the SAC-CI methods. The SAC-CI SD-*R* and general-*R* methods gave almost the same IPs and intensities for these main peaks.

In the inner-valence region, the SAC-CI general-*R* method gave very accurate theoretical spectra for these hydrides. Several unknown satellite peaks were predicted and the detailed assignments were given. For H_2O, we calculated three peaks at about 27, 37 and 41 eV, which have not been detected experimentally. For H_2S, we gave the detailed characterizations for the complicated bands in the energy region of 22–25 eV, observed by SRPES and XPS. A shake-up peak was predicted at around 26 eV. For H_2Se, we proposed detailed outer-and inner-valence satellite peaks. The structure of the satellite spectrum of H_2Se was very similar to that of H_2S. Considerable mixing of the two-electron process with excitations to the Rydberg orbitals was found for the shake-up states of H_2S and H_2Se, in comparison with those of H_2O and we found that the Rydberg basis function is quite important for describing these states.

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